

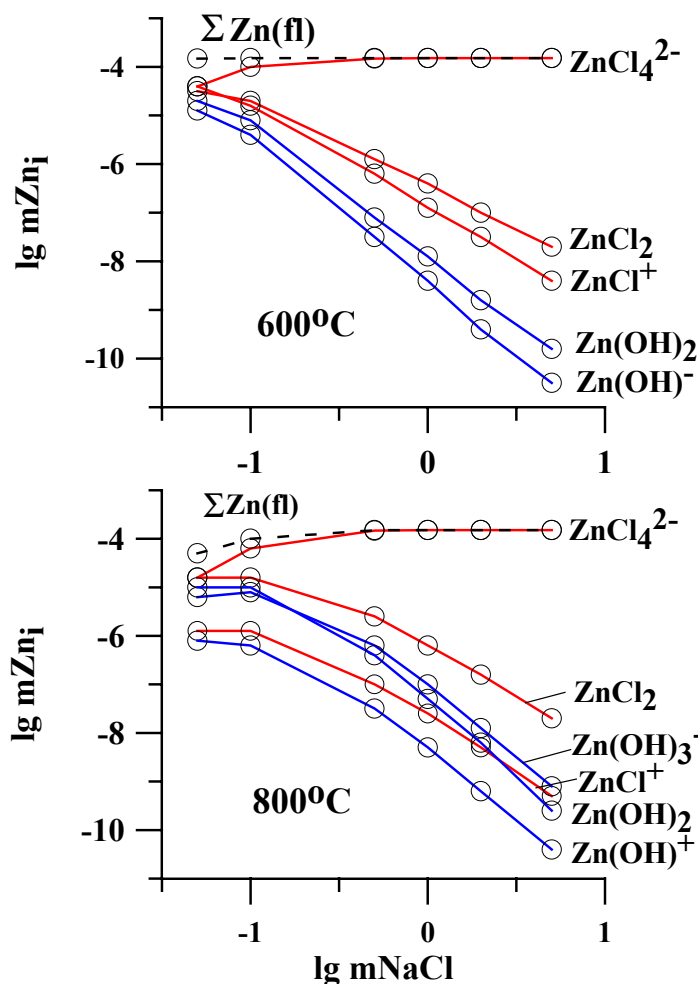
# THERMODYNAMIC SIMULATION OF THE COMPLEX FORMATION IN $\text{ZnO}_{(\text{cr})}(\text{PbO}_{(\text{cr})}) - \text{NaCl}(\text{KCl}, \text{NaCl-HCl}) - \text{H}_2\text{O}$ SYSTEMS AT GRANITOIDIC MAGMA PARAMETERS

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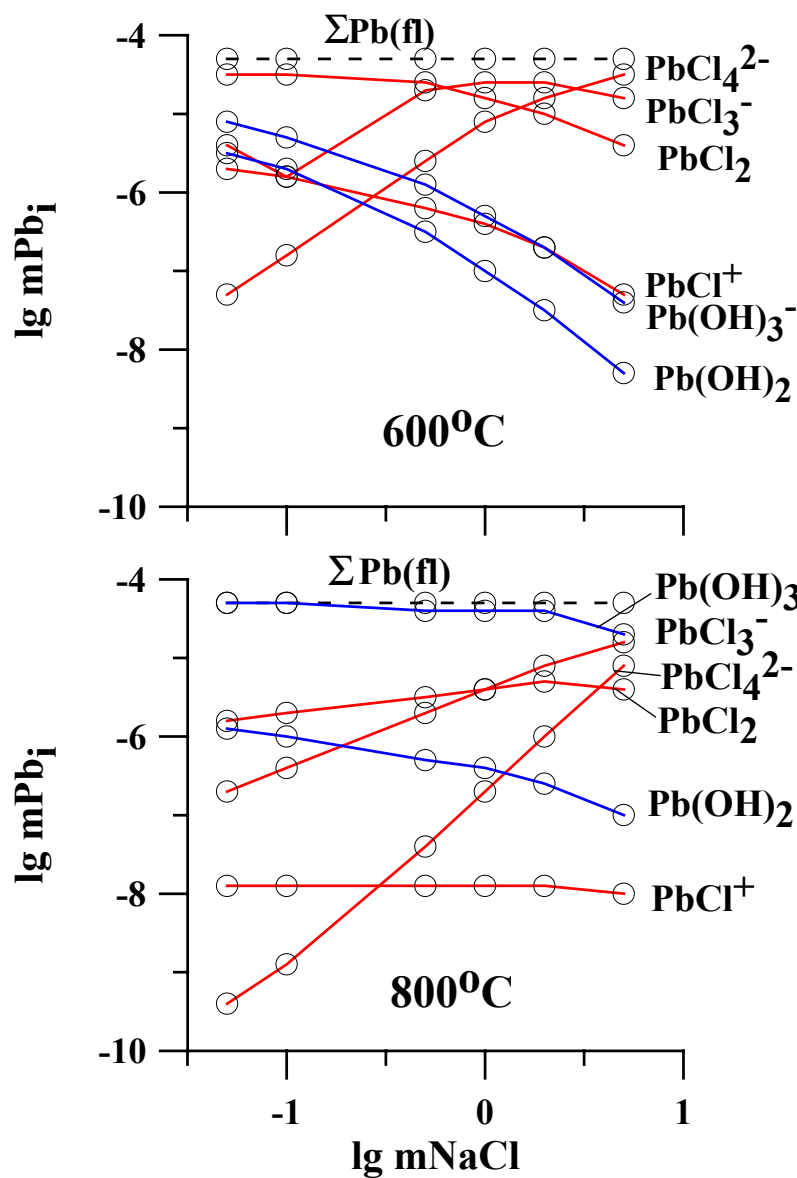
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**Key words:** Thermodynamic simulation, the complex formation, magmatic fluids

Thermodynamic simulation of the complex formation in  $\text{ZnO}_{(\text{cr})}(\text{PbO}_{(\text{cr})}) - \text{NaCl}(\text{KCl}, \text{NaCl-HCl})$  - aqueous solution systems over a wide range of temperatures (from 600 to 900 °C), pressures (from 0,7 to 5 kbars) and  $\text{NaCl}(\text{KCl})$  concentrations (from 0,01 to 5 mol  $\text{kg}^{-1}$ ) has been performed. The aim of the study was to estimate possible Zn - and Pb aqueous species in water chloride fluids under conditions of magmatic fluids formation of granitoidic magmas. We used Shwarov's program complex HCh [1] for computer modeling. The thermodynamic information for dissolved species was obtained using the Shocks model [2] that provides the best fit with experimental data on stability constants for Zn and Pb chloride- and hydroxycomplexes. The free formation energies of solid phases were taken from the thermodynamic database of Holland and Powell [3]. The simulation results show that in Zn-systems  $\text{ZnCl}_4^{2-}$  complex predominates at all studied temperatures (from 600 to 900°C), pressures  $\geq 2$  kbar and chloride concentrations more than 0,5 mol  $\text{kg}^{-1}$ . At lower chloride concentrations  $\text{ZnCl}_2^0$  and  $\text{ZnCl}^+$  -complexes as well hydroxycomplexes  $\text{ZnOH}^+$ ,  $\text{Zn}(\text{OH})_2^0$ ,  $\text{Zn}(\text{OH})_3^-$  are formed along with  $\text{ZnCl}_4^{2-}$  (fig. 1).



**Fig.1.** The concentration dependence of Zn-complex distribution in  $\text{ZnO}_{(\text{cr})} - \text{NaCl} - \text{H}_2\text{O}$  system at 600 and 800°C and 2 kbar (the initial Zn concentration in the system is equal to 10 ppm). Doted line is total Zn concentration in equilibrated fluid ( $\Sigma\text{Zn}_{(\text{fl})}$ ).



**Fig.2.** The concentration dependence of Pb-complex distribution in  $\text{PbO}_{(\text{cr})} - \text{NaCl} - \text{H}_2\text{O}$  system at 600 and  $800^\circ\text{C}$  and 2 kbar (the initial Pb concentration in the system is equal to 10 ppm). Doted line is total Pb concentration in equilibrated fluid ( $\Sigma\text{Pb}_{\text{fl}}$ ).

In Pb-systems under similar conditions the hydroxycomplexes content essentially increases. At temperatures  $\geq 800^\circ\text{C}$  the  $\text{Pb}(\text{OH})_3^-$ -complex predominates practically in all the range of investigated NaCl concentration range. The presence of chloride complexes at these temperatures becomes detectable only at high chloride concentrations (fig. 2). At temperatures  $< 800^\circ\text{C}$  the dominating Pb-species vary in the following manner:  $\text{Pb}(\text{OH})_3^- - \text{PbCl}_2^0 - \text{PbCl}_3^- - \text{PbCl}_4^{2-}$  in accordance with the increasing NaCl concentration. The substitution of NaCl for KCl and the increase of the fluid acidity by addition of HCl leads to the increase of Zn and Pb chloride complexes fractions. The percentage of chloride complexes decreases with temperature increasing and pressure decreasing and also with decreasing of initial chlorine concentration in fluid both for Zn- and for Pb-systems (Table). This trend is more pronounced for the lead bearing systems.

Table.

mNaCl	T °C	600	700	800	900	600	700	800	900
	P, kbar	10 ppm Zn				1000 ppm Zn			
0.05	5	91	100	100	100	60	81	92	96
	2	74	80	68	28	74	81	69	29
	1	48	30	7	1	48	30	7	2
	0.7	44				44			
5	5	100	100	100	100	100	100	100	100
	2	100	100	100	100	98	97	92	90
	1	100	100	50	40	87	89	49	49
	0.7	97				95			
		10 ppm Pb				1000ppm Pb			
0.05	5	99	96	81	33	40	41	40	33
	2	77	36	3	0	33	31	21	5
	1	31	16	3	0	21	18	8	2
	0.7	24				11			
5	5	100	100	100	96	79	81	82	78
	2	100	97	55	4	63	51	37	20
	1	99	90	48	2	42	45	38	15
	0.7	98				66			

Total percentage of Zn and Pb chloride complexes in equilibrated fluid of the  $\text{ZnO}_{(\text{cr})}(\text{PbO}_{(\text{cr})}) \text{NaCl} - \text{H}_2\text{O}$  systems (mol.%). Calculation results are given for the systems containing 10 and 1000 ppm of metals.

Shaded sections of table correspond to the fluid heterogeneous region.

The results obtained may be used for interpretation of the experimental data on Zn and Pb distribution between aqueous chloride fluid and granitic melt.

*This work was supported by Earth Sciences Department of RAS, project 10-5, 2003.*

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*Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21) 2003*  
*Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003*  
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 Published on July 15, 2003

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